Microphase separation at two length scales

Nap, R.J.; Kok, C.; Brinke, G. ten; Kuchanov, S.I.

Published in:
The European Physical Journal E

DOI:
10.1007/s101890170106

Publication date:
2001

Eur. Phys. J. E **4**, 515–519 (2001)

THE EUROPEAN PHYSICAL JOURNAL E

EDP Sciences

Microphase separation at two length scales

R.J. Nap[1,a], C. Kok[1], G. ten Brinke[1], and S.I. Kuchanov[2]

[1] Department of Polymer Chemistry and Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

[2] Keldysh Institute of Applied Mathematics of the Russian Academy of Sciences, Miusskaya Square 4, Moscow 125047, Russia

Received 25 August 2000

Abstract. The possibility of microphase separation at two different length scales in monodisperse AB block copolymer melts consisting of a homopolymer A block and either a linear alternating AB copolymer block (poly$(A)_m$-*block*-poly(B-*alt* -$A)_n$) or an AB comb copolymer block poly$(A)_m$-*block*-poly(A-*graft*-$B)_n$, is investigated. An analysis of the structure factor reveals that in the parameter space of n and m three different cases can be distinguished: I) The structure factor has only one minimum corresponding to the short length scale (*i.e.* the characteristic length of the repeating unit of the alternating or comb block). II) The structure factor has only one minimum corresponding to the long length scale (the characteristic length of the blocks). III) Two minima are present leading to a competition between microphase separation at the short and the long length scale. Depending on the choice of n and m, one of these three possibilities will occur.

PACS. 36.20.-r Macromolecules and polymer molecules – 64.60.Cn Order-disorder transformations, statistical mechanics of model systems

1 Introduction

Diblock copolymer melts usually microphase separate with *one* characteristic length. If more than two monomer types are involved, microphase separation frequently occurs at more than one length scale [1–5].

However, this phenomenon is not restricted to block copolymers involving three or more chemically different monomers. To demonstrate and analyze this, we studied the structure factor of two sets of block copolymers consisting of a homopolymer A block linked to either an AB comb copolymer or to a linear alternating AB copolymer, see Figure 1.

Due to the architecture of the molecules microphase separation can occur at two different length scales, either "inside" the AB block or "between" the homopolymer A block and the AB block, see Figure 2. In the latter case the behavior resembles that of a diblock copolymer, where one block is the homopolymer A block and the other block the AB comb or alternating block.

The paper is organized as follows. In Section 2 the pertinent system parameters are defined, in Section 3 the theory is outlined and in Section 4 the results are discussed.

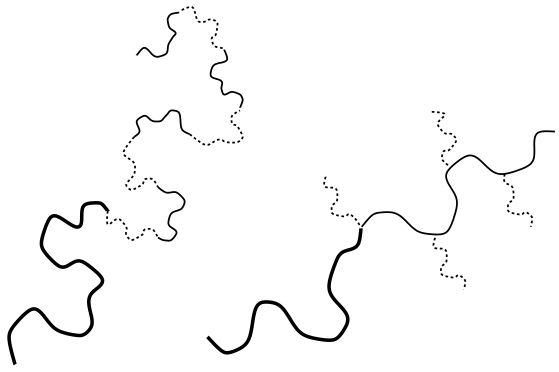

Fig. 1. Model of the two molecules studied in this paper.

2 Model

The poly$(A)_m$-*block*-poly(A-*graft*-$B)_n$ polymer will be considered first. The AB comb copolymer block has a backbone consisting of monomers of type A to which side chains consisting of monomers of type B are attached. The number of backbone segments is $N_A^{\rm b}$, that of each side chain equals N_B. Monomers A and B are assumed to be of equal size. We assume that all branch points have the same functionality $z = \alpha+2$, where α is the number of side chains per branch point. Furthermore, the branch points are distributed regularly. The number of branch points is denoted by n. Therefore, the number of side chains is given by $n_{\rm s} = \alpha n$. The number of backbone segments between

[a] e-mail: nap@chem.rug.nl

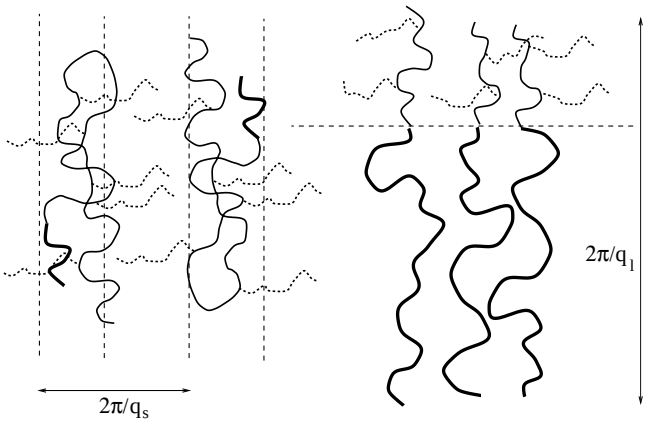

Fig. 2. Illustration of the two ways in which the system can microphase separate.

successive side chains is $N_A^{\rm b}/n$. The number of backbone segments before the first side chain plus those after the last side chain also add up to $N_A^{\rm b}/n$. Therefore, the number of backbone segments before the first side chain and those after the last side chain will be $tN_A^{\rm b}/n$ and $(1-t)N_A^{\rm b}/n$, respectively, where $t \in [0,1]$ is called the asymmetry parameter [6]. The number of homopolymer A segments is denoted by $N_A^{\rm h}$.

To simplify the discussion, we assume that $N_B = N_A^{\rm b}/n = d$, $N_A^{\rm h} = md$, $t = 0$ and $\alpha = 1$. Then the total number of segments will be equal to $N = N_A^{\rm h} + N_A^{\rm b} + n_{\rm s}N_B = md + nd + nd = (m+2n)d$.

The parameterization of the poly$(A)_m$-*block*-poly(*B*-*alt* -*A*)$_n$ polymer is similar, of course without the parameters α and t. Here we also take $N_B = N_A^{\rm b}/n = d, N_A^{\rm h} = md$. See Figure 1.

An important quantity is the volume fraction $f_{\rm h}$ of the homopolymer block A, which is equal to $f_{\rm h} = m/(m+2n)$.

3 Theory

We use the weak segregation theory to analyze the microphase separation [7,8]. The weak segregation theory is based on a free energy expansion in powers of the order parameter, $\psi(q)$, where $\psi(q)$ is the Fourier transform of $\psi(r)$, which equals the excess volume fraction of A monomer at position r. The second-order expansion term is proportional to the inverse of the structure factor $S(q) = \langle\psi(q)\psi(-q)\rangle$,

$$S^{-1}(q) = \frac{\sum G_{\alpha\beta}}{\det G} - 2\chi = H(q) - 2\chi\,, \qquad (1)$$

where $G_{\alpha\beta}$ are the second-order correlation functions, $\alpha, \beta = (A, B)$ and χ the Flory-Huggins parameter. Furthermore, the structure factor is proportional to the scattering intensity.

For an inverse length, q, for which $S^{-1}(q)$ becomes negative, fluctuations of $\psi(q)$ will be enhanced. Hence the inverse structure factor determines the instability of the homogeneous or isotropic phase ($\psi = 0$), *i.e.* the spinodal. The spinodal corresponds to the locus of points in phase space where the isotropic phase ($\psi = 0$) becomes unstable against fluctuations, *i.e.* macro/microphase separation. It is given by

$$\left.\frac{\partial S^{-1}(q)}{\partial q}\right|_{q^*} = 0 \quad \text{and} \quad \left.\frac{\partial^2 S^{-1}(q)}{\partial q^2}\right|_{q^*} > 0 \quad \text{and}$$
$$(\chi N)_{\rm s} = NH(q^*)/2\,, \qquad (2)$$

where q^* is the critical inverse length and N the total number of segments. The value of q^* is determined by the position of the minimum of $S^{-1}(q)$. Because q is the inverse length, q^* will be a measure of the length scale of phase separation of the system.

With $G_{\alpha\beta} = \tilde{G}_{\alpha\beta}d^2/N$ and $\xi = a^2q^2d/6$, where a is the Kuhn length, the correlation functions for the poly$(A)_m$-*block*-poly(A-*graft* -B)$_n$ are

$$\tilde{G}_{AA} = (n+m)^2 g((n+m)\xi), \qquad (3)$$
$$\tilde{G}_{AB} = n\alpha[(n-1)z_n(\xi) + h(n\xi)\{(m+t)h((m+t)\xi) + (1-t)h((1-t)\xi)\}], \qquad (4)$$
$$\tilde{G}_{BB} = n\alpha[g(\xi) + (n-1)\alpha e^{-\xi}z_n(\xi) + (\alpha-1)h(\xi)^2]. \qquad (5)$$

Similarly, for the poly$(A)_m$-*block*-poly(B-*alt* -A)$_n$ they are given by

$$\tilde{G}_{AA} = \big[ng(\xi) + m^2 g(m\xi) + ne^{-\xi}\phi(\xi)\{(n-1)\phi(\xi)z_n(2\xi) + 2mh(m\xi)h(2n\xi)\}\big]\,, \qquad (6)$$
$$\tilde{G}_{AB} = n\phi(\xi)[mh(m\xi)h(2n\xi) + \phi(\xi)\{h(2\xi)h(2n\xi) + (n-1)z_n(2\xi)\}], \qquad (7)$$
$$\tilde{G}_{BB} = n[g(\xi) + (n-1)e^{-\xi}\phi(\xi)^2 z_n(2\xi)]\,, \qquad (8)$$

where

$$g(x) = \frac{2}{x^2}(-1 + x + e^{-x}), \qquad (9)$$
$$h(x) = [1 - e^{-x}]/x, \qquad (10)$$
$$z_n(x) = 2[h(x) - h(nx)]/[(n-1)x], \qquad (11)$$
$$\phi(x) = \frac{h(x)}{h(2x)} = \frac{2}{1+e^{-x}}. \qquad (12)$$

Because the two polymer melts under consideration are monodisperse, only microphase separation can occur, *i.e.* $q^* > 0$. Furthermore, they have two intrinsic length scales. See Figure 2. The system favors microphase separation on the inverse length scale q^*, which corresponds to the lowest critical $(\chi N)_{\rm s}$ value. This is given by the absolute minimum of $S^{-1}(q)$.

The two different inverse length scales are denoted by $q_{\rm s}^*$ and $q_{\rm l}^*$. The inverse length scale $q_{\rm s}^*$ belongs to the intrinsic length scale of the AB block and the inverse length scale $q_{\rm l}^*$ belongs to the length scale between the AB block and the A block. There are five different possibilities. The inverse structure factor has either one minimum at $q_{\rm s}^*$ or $q_{\rm l}^*$, or it has two minima at $q_{\rm s}^*$ and $q_{\rm l}^*$. In the latter case, either $S^{-1}(q_{\rm s}^*)$ or $S^{-1}(q_{\rm l}^*)$ corresponds to the absolute minimum or both minima are equal, *i.e.* $S^{-1}(q_{\rm s}^*) = S^{-1}(q_{\rm l}^*)$.

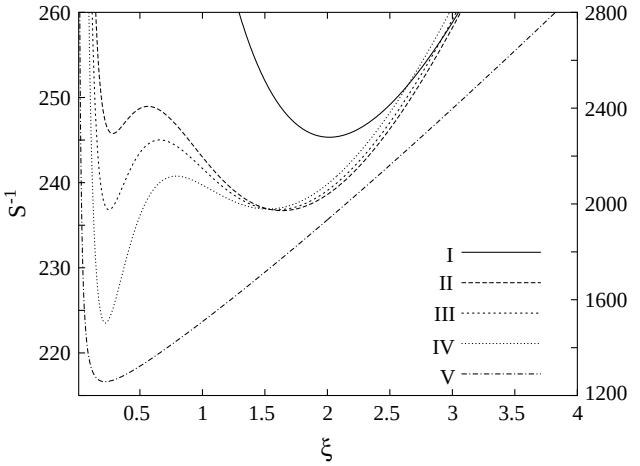

Fig. 3. The inverse structure factors of the comb copolymer for I $(n,m) = (21,3)$, II $(n,m) = (20,5.5)$, III $(n,m) = (20,5.69)$, IV $(n,m) = (20,6)$ and V $(n,m) = (1,44)$. The right y-axis correspond to V. For I and V there is only one minimum at $q_{\rm s}^*$ and $q_{\rm l}^*$, respectively. For II and IV there are two minima with the absolute minimum at $q_{\rm s}^*$, respectively, $q_{\rm l}^*$. For III the two minima are equal. Note that $\xi = a^2q^2d/6$.

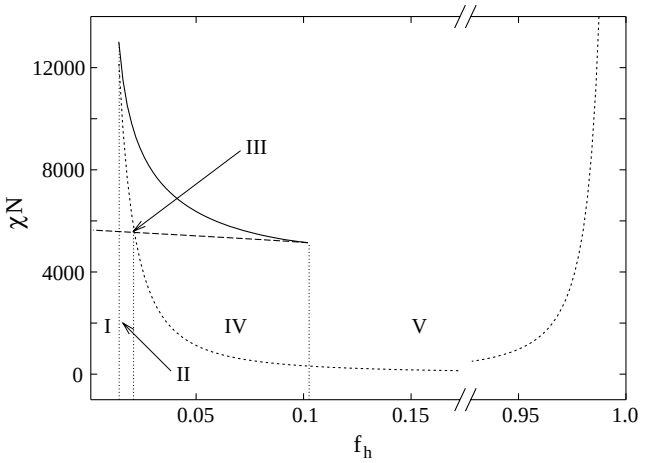

Fig. 4. χN *versus* $f_{\rm h}$ with $2n + m = 1000$. The dotted line corresponds to $S^{-1}(q_{\rm l}^*)$, the dashed line to $S^{-1}(q_{\rm s}^*)$ and the solid line to the maximum of $S^{-1}(q)$.

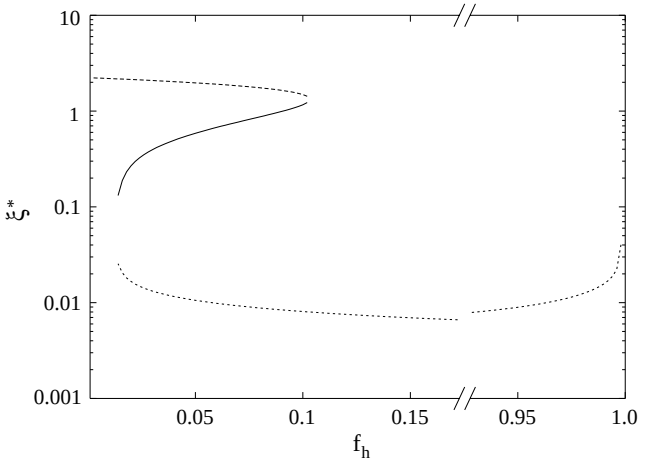

Fig. 5. ξ^* *versus* $f_{\rm h}$ with $2n + m = 1000$. Note that $\xi = a^2q^2d/6$. The dotted line corresponds to $q_{\rm l}^*$, the dashed line to $q_{\rm s}^*$ and the solid line to the value of q for which $S^{-1}(q)$ has a maximum.

4 Results and discussion

The results discussed below, correspond to the comb copolymer system with $\alpha = 1$ and $t = 0$, unless stated otherwise.

In Figure 3 the inverse structure factor is plotted for the five different possibilities. For any value of n and m the behavior of $S^{-1}(q)$ will correspond to one of these curves.

The spinodal χN is a function of two independent variables n and m or an arbitrary combination thereof. This is unlike the spinodal of, *e.g.*, a diblock copolymer melt where there is only one composition variable and the spinodal is usually given as a function of the volume fraction f_A.

In order to construct the spinodal, a convenient choice of variables must be made. For this we take $f_1 = m+2n = N/d$ and $f_2 = m/(m+2n) = f_{\rm h}$. When f_1 is taken to be constant and χN is plotted against f_2, the corresponding spinodal can be given the usual "diblock" interpretation. By keeping f_1, thus N, constant, a change of χN will be caused only by the variation of the composition and the architecture and not by a change of the number of monomers N. This has an advantage over the more obvious choice of $f_1 = n$ and $f_2 = m$. In that case, when either f_1 or f_2 is taken to be constant and the other varied, N will also change.

A representative spinodal is plotted in Figure 4. The two broken lines correspond to the two minima and the solid line corresponds to the maximum of S^{-1}. Furthermore, we have indicated where the five different cases of the inverse scattering function occur along the spinodal curve.

When the volume fraction of the homopolymer block A, $f_{\rm h}$, is small, the phase behavior is governed by the comb block only. Thus microphase separation occurs at $q^* = q_{\rm s}^*$.

When $f_{\rm h}$ increases, the second minimum in $S^{-1}(q)$, corresponding to $q_{\rm l}^*$, appears. Upon increasing $f_{\rm h}$, m becomes larger and n smaller, thereby increasing the length of the homopolymer block and reducing the length of the comb block. The "diblock" structure formed by the homopolymer block and the comb block becomes more symmetric where upon the critical $(\chi N)_{\rm s}^{\rm l}$ value and corresponding inverse length scale $q_{\rm l}^*$ decrease [7], see Figures 4 and 5. However, the change of n has little effect on the critical $(\chi N)_{\rm s}^{\rm s}$ value and its inverse length scale $q_{\rm s}^*$ of the AB comb block, because the length of microphase separation is dominated by the repeating unit of the comb block. A change of n has a noticeable effect on the phase behavior only when the number of repeating units, n, is small $(n \lesssim 10)$ [9,10].

When $f_{\rm h}$ has increased sufficiently, $S^{-1}(q_{\rm l}^*)$ becomes smaller than $S^{-1}(q_{\rm s}^*)$. Now, the phase behavior involves separation between the homopolymer block and the comb

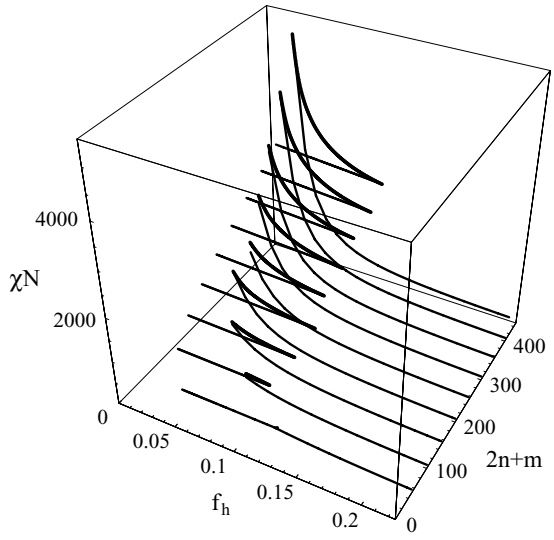

Fig. 6. Plot of χN *versus* $f_{\rm h} = \frac{m}{2n+m}$ for various values of $2n + m$.

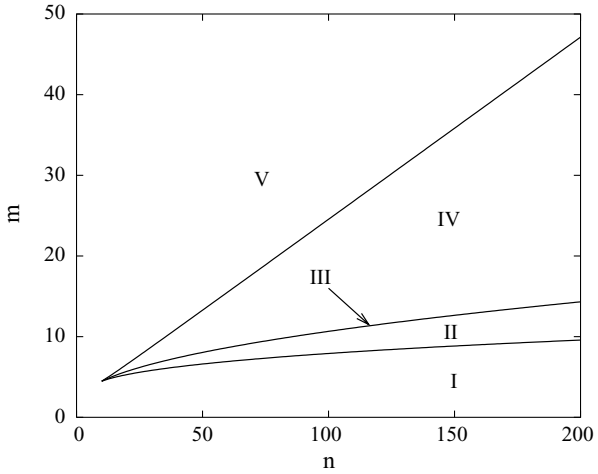

Fig. 7. Plot of n *versus* m.The lines correspond to the boundaries between the different regions in which a particular situation occurs. Case III is a line (not a region). The numbers correspond to the classification given in Figure 3.

block. Upon further increasing $f_{\rm h}$ the minimum in $S^{-1}(q)$ corresponding to $q_{\rm s}^*$ disappears.

Finally, when $f_{\rm h}$ approaches unity, the polymer corresponds effectively to a very asymmetric diblock copolymer. Consequently, $(\chi N)_{\rm s}^{\rm l}$ will increase again.

Note that n can have only positive integer values, $n \in \mathbb{N}$, whereas m is allowed to have any positive value, $m \in \mathbb{R}^+$. Therefore, the spinodal in Figure 4 is a set of points. However because $f_1 = 2n + m = 1000$ is large, there are sufficiently many points to present the spinodal as a line.

To classify the behavior in the parameter space of n and m Figures 6 and 7 are given. In Figure 6 the spinodal χN *versus* $f_{\rm h}$ is plotted for different values of f_1.

Regions II and IV disappear for small values of f_1. This can also be seen from Figure 7, which is a projection of Figure 6 onto the (n, m)-plane, where the lines indicate

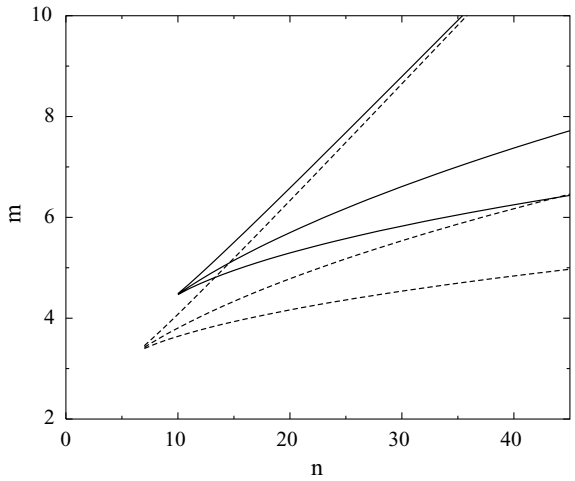

Fig. 8. Plot of n *versus* m for the comb-coil molecule (solid lines) and the alternating-coil molecule (dashed lines).

the boundaries between the different regions. In relation to the spinodal of Figure 4 the points, making up the lines of Figure 7, correspond to the end points of the maximum curve and point III. At $n^* = 10$ and $m^* = 4.467$ the boundary lines converge and below that point the lines are absent. The point (n^*, m^*) can be viewed as a bifurcation point in the parameter space. It correspond to a threshold in the parameter space, below which only microphase separation at *one* length scale can occur; above it microphase separation is possible at *two* different length scales.

The use of different values for α and t will lead to different values for, *e.g.*, the bifurcation point. The same holds for the alternating-coil copolymer. However, the overall behavior remains similar as illustrated in Figure 8.

5 Concluding remarks

In this paper we described the phase behavior of polymer systems having two intrinsic length scales. By varying the system parameters, microphase separation can occur at only one or at both length scales. We established that there is a bifurcation point below which microphase separation occurs only at one length scale. Above the bifurcation point two length scales are possible and the choice of the parameters determines which length scale is favored. Of course, at sufficiently low temperatures both length scales might be present as observed experimentally [1–3].

The most interesting case corresponds to line III, where the two minima of $S^{-1}(q)$ are equal. Here, the structure appearing at the order-disorder transition will involve both length scales. Its theoretical description based on a Landau free energy expansion up to fourth order likewise requires the two wave vectors. This will be addressed in a future publication.

References

1. J. Ruokolainen, R. Mäkinen, M. Torkkeli, T. Mäkelä, R. Serimaa, G. ten Brinke, O. Ikkala, Science **280**, 557 (1998).
2. J. Ruokolainen, G. ten Brinke, O. Ikkala, Adv. Mater. **11**, 777 (1999).
3. J. Ruokolainen, M. Saariaho, O. Ikkala, G. ten Brinke, E.L. Thomas, M. Torkkeli, R. Serimaa, Macromolecules **32**, 1152 (1999).
4. U. Breiner, U. Krappe, V. Abetz, R. Stadler, Macromol. Chem. Phys. **198**, 1051 (1997).
5. A. Werner, G.H. Fredrickson, J. Polym. Sci. B: Polym. Phys. **35**, 849 (1997).
6. A. Shinozaki, D. Jasnow, A.C. Balazs, Macromolecules **27**, 2496 (1994).
7. L. Leibler, Macromolecules **13**, 1602 (1980).
8. R. Holyst, T.A. Vilgis, Macromol. Theory Simul. **5**, 573 (1996), cond-mat/960306.
9. D.P. Foster, D. Jasnow, A.C. Balazs, Macromolecules **28**, 3450 (1995).
10. H. Benoit, G. Hadziioannou, Macromolecules **21**, 1449 (1988).